

## MECHANISMS OF ION ADSORPTION IN SOILS: GENERAL

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Adsorption is the net accumulation of a chemical entity at the interface between a solid phase and an aqueous solution phase (Sposito, 1989). This accumulation is restricted to a two-dimensional molecular structure on the surface. The chemical entity that accumulates at the interface is called the adsorbate, while the surface on which accumulation takes place is called the adsorbent. Adsorption reactions in soils can be described by a variety of models. Empirical models provide descriptions of experimental adsorption data without theoretical basis. Chemical models, on the other hand, provide a molecular description of adsorption using an equilibrium approach.

The purpose of this paper is to review various models used to describe ion adsorption in soils. First, I will describe common empirical models used in soil chemistry and evaluate their limitations. Second, I will present common chemical models used to describe adsorption on soil minerals and discuss their advantages over the empirical approaches. Last, I will describe limitations and approximations in the use of these chemical models in soil systems.

## EMPIRICAL MODELS

Adsorption reactions in soils have historically been described using empirical isotherm equations. Such equations are typically very good at describing experimental data despite their lack of theoretical basis. Popularity of the isotherm equations stems in part from their simplicity and the ease of estimation of their adjustable parameters.

### Distribution Coefficient

The simplest and most widely used adsorption isotherm equation is linear. Such an isotherm is conventionally expressed in terms of the distribution coefficient,  $K_d$ :

$$x = K_d c \quad (1)$$

where  $x$  is the amount of ion adsorbed per unit mass and  $c$  is the equilibrium solution ion concentration. Distribution coefficients have been used widely to describe contaminant adsorption in flowing systems (Reardon, 1981) and in transport models (Travis and Etnier, 1981). Because of the linear assumption, the distribution coefficient usually describes ion adsorption data only over a very restricted solution concentration range.

### Langmuir Isotherm Equation

The Langmuir adsorption isotherm equation was developed to describe the adsorption of gases onto clean solids and can be derived theoretically based on rates of evaporation and condensation. The isotherm equation is:

$$x = \frac{x_m Kc}{1 + Kc} \quad (2)$$

where  $x_m$  is the maximum adsorption per unit mass and  $K$  is an affinity parameter related to the bonding energy of the surface. The Langmuir isotherm implies a finite number of uniform adsorption sites and absence of lateral interactions. Despite the fact that its assumptions are violated in soils, the Langmuir equation has often been used to describe ion adsorption on soils and soil minerals. For many studies the Langmuir isotherm equation could only describe adsorption for low solution ion concentrations.

#### Multi-Surface Langmuir Adsorption Isotherm Equation

The Langmuir adsorption isotherm equation was also formulated for the simultaneous adsorption of a gas by more than one surface. This expression is:

$$x = \sum_{i=1}^n \frac{x_{m_i} K_i c}{1 + K_i c} \quad (3)$$

where  $n$  is the number of sets of surface sites. Because of the increase in the number of adjustable parameters, fit to ion adsorption data with the multi-surface Langmuir isotherm is usually excellent.

#### Freundlich Adsorption Isotherm Equation

The Freundlich adsorption isotherm equation is the oldest of the nonlinear isotherms and implies heterogeneity of adsorption sites. The isotherm equation is:

$$x = Kc^\beta \quad (4)$$

where  $\beta$  is a heterogeneity parameter, the smaller  $\beta$  the greater the expected heterogeneity (Kinniburgh, 1985). The Freundlich adsorption isotherm reduces to a linear adsorption isotherm when  $\beta = 1$ . Despite the fact that the Freundlich equation is strictly valid only for adsorption at low concentration (Sposito, 1984), it has often been used to describe ion adsorption by soils over the entire concentration range studied. The Freundlich isotherm does not obey Henry's law at low concentration nor does it reach an adsorption maximum at high concentration (Kinniburgh, 1985).

#### Temkin Adsorption Isotherm Equation

The Temkin adsorption isotherm equation results when the energy of adsorption is a linear function of the surface coverage (Travis and Etnier, 1981). The isotherm equation is:

$$x = a + b \log c \quad (5)$$

where  $a$  and  $b$  are parameters. The Temkin isotherm is only valid over an intermediate range

of concentrations (Kinniburgh, 1985).

#### Toth Adsorption Isotherm Equation

The Toth adsorption isotherm equation obeys Henry's law at low concentration and reaches an adsorption maximum at high concentration (Kinniburgh, 1985). The isotherm equation is:

$$x = \frac{x_m Kc}{[1 + (Kc)^\beta]^{1/\beta}} \quad (6)$$

The Toth adsorption isotherm reduces to the Langmuir adsorption isotherm when  $\beta = 1$  (Kinniburgh, 1985).

#### Dubinin-Radushkevich Adsorption Isotherm Equation

The Dubinin-Radushkevich adsorption isotherm equation is:

$$\log x = -\beta [\log(Kc)]^2 + \log x_m \quad (7)$$

This isotherm is suitable only for an intermediate range of concentrations because of its unrealistic asymptotic behavior (Kinniburgh, 1985).

### LIMITATIONS OF THE EMPIRICAL APPROACH

Although theoretically impossible, the Langmuir isotherm equation can describe experimental data from a precipitation reaction (Veith and Sposito, 1977). For the Langmuir adsorption isotherm equation, Sposito (1982) has developed two theorems. The mechanism theorem states that the adherence of experimental data to the Langmuir isotherm gives no information concerning the chemical mechanism of the reaction. The interpolation theorem states that any reaction for which  $K_d$  is a finite, decreasing function of the amount adsorbed,  $x$ , and extrapolates to zero at a finite value of  $x$ , can be represented mathematically by a two-surface Langmuir isotherm.

Although the above isotherm equations are often excellent at describing ion adsorption they are simply numerical relationships used to describe data. Independent experimental evidence for adsorption must be present before any chemical meaning can be assigned to the isotherm equation parameters. Since the use of the adsorption isotherm equations constitutes essentially a curve-fitting procedure, the parameters are valid only for the conditions under which the experiment was conducted. Prediction of ion adsorption behavior under changing conditions of solution pH, ionic strength, and solution ion concentration is impossible.

### Linear Transformations

The Langmuir and the Freundlich adsorption isotherm can be transformed to linear form allowing their parameters to be estimated graphically or by linear regression. The various linear transformations of the Langmuir equation result in:

(1) the reciprocal Langmuir plot:

$$\frac{c}{x} = \frac{1}{x_m K} + \frac{c}{x_m} \quad (8)$$

(2) the distribution coefficient or Scatchard plot:

$$\frac{x}{c} = x_m K - xK \quad (9)$$

(3) the Eadie-Hofstee plot:

$$x = x_m - \frac{x}{K} \quad (10)$$

(4) the double reciprocal or Lineweaver-Burk plot:

$$\frac{1}{x} = \frac{1}{x_m} + \frac{1}{x_m K} \quad (11)$$

Each of these linear transformations changes the original error distribution by weighting low adsorption values more than high adsorption values (Kinniburgh, 1986). The reciprocal Langmuir plot is the linearization most commonly used by soil scientists. Dowd and Riggs (1965) found the reciprocal Langmuir plot to be less sensitive in detecting deviations from linearity than the Eadie-Hofstee plot. An additional disadvantage of the Eadie-Hofstee, as well as the Scatchard plots is that they use  $x$ , which is usually assumed to contain all of the measurement error, as the independent variable which is assumed to be error free in conventional regression analysis (Kinniburgh, 1986). The best linear transformation is not necessarily the one that gives the highest correlation coefficient but rather the one where the error distribution most closely matches the true error distribution (Kinniburgh, 1986).

The linear form of the Freundlich equation is:

$$\log x = \log K + \beta \log c \quad (12)$$

The insensitivity of the linear form is at least partially responsible for the frequent good fit of data to the Freundlich equation. Log-log plots, such as the linear form of the Freundlich isotherm are well known for their insensitivity. An additional disadvantage is that all data points are not given equal weightings in the analysis of log-transformed values (Barrow, 1978).

### Nonlinear Least Squares Methods

For the Temkin, Toth, and Dubinin-Radushkevich isotherms, containing three parameters, it is not possible to estimate the parameters by linear regression or any reliable graphical method. Nonlinear regression is necessary to fit these isotherms. Nonlinear regression usually involves the minimization of residual sums of squares, an operation which is no longer computationally difficult because of the wide availability of computer algorithms (Kinniburgh, 1986). Direct fitting of adsorption data using nonlinear least squares methods avoids the difficulties of changes in error distribution and biased parameters associated with linear transformations. However, use of linear regression of any linear form with proper weighting can provide parameter estimates close to those obtained with nonlinear least squares methods (Kinniburgh, 1986).

Use of nonlinear least squares methods involves finding the set of parameters that minimizes the weighted residual sum of squares, WRSS, given by (Kinniburgh, 1986):

$$WRSS = \sum_{i=1}^m w_i (n_i - \hat{n}_i)^2 \quad (13)$$

where  $\hat{n}_i$  is the fitted value for observation  $i$ ,  $w_i$  is the weighting factor, and  $m$  is the number of observations (Kinniburgh, 1986). The computer program ISOTHERM (Kinniburgh, 1985) contains nonlinear least squares routines for fitting numerous adsorption isotherm equations including the ones listed above. The principal criterion to compare the goodness-of-fit of different isotherms to the same data set is the coefficient of determination,  $R^2$  defined by (Kinniburgh, 1985):

$$R^2 = \frac{RSS}{TSS} \quad (14)$$

where RSS is the residual sum of squares defined by:

$$RSS = \sum_{i=1}^m (n_i - \hat{n}_i)^2 \quad (15)$$

and TSS is the corrected total sum of squares defined by:

$$TSS = \sum_{i=1}^m (n_i - \bar{n})^2 \quad (16)$$

where  $\bar{n}$  is the mean value of  $n_i$ . Nonlinear fitting of adsorption data can result in much improved values of the coefficient of determination over linear transformations (Goldberg and Forster, 1991).

### CHEMICAL MODELS

Various chemical surface complexation models have been developed to describe potentiometric titration and ion adsorption data at the oxide-mineral solution interface.

Surface complexation models provide molecular descriptions of ion adsorption using an equilibrium approach defining surface species, chemical reactions, mass balances, and charge balance. Thermodynamic properties such as activity coefficients and equilibrium constants are calculated mathematically. The major advancement of the surface complexation models is the consideration of charge on both the adsorbing ion and the adsorbent surface. Despite extensive application of these models to reference oxide minerals, their use to describe ion adsorption in soils has been limited. I will discuss the three models that have been applied to soil systems.

#### Balance of Surface Charge

The balance of surface charge on a soil particle in solution is defined by (Sposito, 1984):

$$\sigma_s + \sigma_H + \sigma_{is} + \sigma_{os} + \sigma_d = 0 \quad (17)$$

where  $\sigma_s$  is the permanent charge resulting from isomorphous substitution in soil minerals,  $\sigma_H$  is the net proton charge resulting from the formation of inner-sphere surface complexes between protons and hydroxyl ions and surface functional groups,  $\sigma_{is}$  is the charge resulting from the formation of inner-sphere complexes between ions, other than protons and hydroxyls, and surface functional groups,  $\sigma_{os}$  is the charge resulting from the formation of outer-sphere complexes with surface functional groups or ions in inner-sphere complexes,  $\sigma_d$  is the dissociated charge equal to minus the surface charge neutralized by background electrolyte ions in solution.

An inner-sphere surface complex contains no water between the adsorbing ion and the surface functional group. An outer-sphere complex, on the other hand, contains at least one water molecule between the adsorbing ion and the surface functional group. Inner-sphere surface complexation of ions is termed specific adsorption, or specifically for anion adsorption, ligand exchange. Outer-sphere surface complexation is termed nonspecific adsorption. The surface functional group is defined as XOH, where X represents a metal ion of the oxide mineral surface bound to a reactive surface hydroxyl group. In the application of surface complexation models to clay and soil systems, the surface functional group can also be an aluminol or silanol group at the edge of a clay mineral particle.

#### Constant Capacitance Model

The constant capacitance model of the oxide-solution interface was developed in Switzerland (Schindler and Gamsjäger, 1972; Hohl and Stumm, 1976; Schindler et al., 1976; Stumm et al., 1976, 1980). The model contains the following assumptions:

- (1) all surface complexes are inner-sphere complexes
- (2) no surface complexes are formed with ions from the background electrolyte
- (3) the Constant Ionic Medium Reference State determines the activity coefficients of the aqueous species
- (4) surface complexes exist in a chargeless environment in the Standard State
- (5) the relationship between surface charge,  $\sigma$ , and surface potential,  $\psi$ , is

linear and given by:

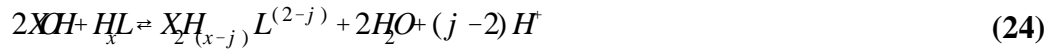
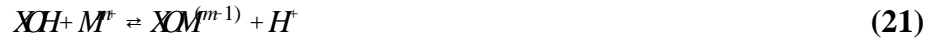
$$\sigma = \frac{CSa}{F}\psi \quad (18)$$

where C is the capacitance (F m<sup>-2</sup>), S is the surface area (m<sup>2</sup> g<sup>-1</sup>), a is the suspension density (g L<sup>-1</sup>), σ has units of mol<sub>c</sub> L<sup>-1</sup>, F is the Faraday constant (C mol<sub>c</sub><sup>-1</sup>), and ψ has units of V.

The protonation and dissociation reactions of the surface functional group are:



The surface complexation reactions for ion adsorption are:



where M represents a metal ion, m+ is the charge on the metal ion, L represents a ligand, x is the number of protons present in the undissociated form of the ligand, 1 ≤ i ≤ n, and 2 ≤ j ≤ n where n is the number of ligand surface complexes and is equal to the number of dissociations undergone by the ligand.

The equilibrium constants describing the above reactions are:

$$K_+(int) = \frac{[XH_2^+]}{[XH][H^+]} \exp[F\psi/RT] \quad (25)$$

$$K_-(int) = \frac{[XO^-][H^+]}{[XH]} \exp[-F\psi/RT] \quad (26)$$

$$K_M^1(int) = \frac{[XOM^{(m-1)}][H^+]}{[XH][M^*]} \exp[(m-1)F\psi/RT] \quad (27)$$

$$K_M^2(int) = \frac{[(XO)_2M^{(m-2)}][H^+]^2}{[XH]^2[M^*]} \exp[(m-2)F\psi/RT] \quad (28)$$

$$K_L^i(int) = \frac{[XH_{(x-i)}L^{(1-i)}][H^+]^{(i-1)}}{[XH][H_xL]} \exp[(1-i)F\psi/RT] \quad (29)$$

$$K_L^j(int) = \frac{[XH_{2(x-j)}L^{(2-j)}][H^+]^{(j-2)}}{[XH]^2[H_xL]} \exp[(2-j)F\psi/RT] \quad (30)$$

where R is the molar gas constant (J mol<sup>-1</sup> K<sup>-1</sup>), T is the absolute temperature (K), and square brackets represent concentrations (mol L<sup>-1</sup>). The electrostatic potential terms  $\exp(-F\psi_i/RT)$  are coulombic correction factors that account for the effect of surface charge on surface complexation and can be considered as solid phase activity coefficients.

The mass balance for the surface functional group is:

$$\begin{aligned} [XH]_T &= [XH] + [XH_2^+] + [XO^-] + [XOM^{(m-1)}] + 2[(XO)_2M^{(m-2)}] \\ &+ \sum_{i=1}^n [XH_{(x-i)}L^{(1-i)}] + \sum_{j=2}^n 2[XH_{2(x-j)}L^{(2-j)}] \end{aligned} \quad (31)$$

and the charge balance is:

$$\begin{aligned} \sigma &= [XH_2^+] - [XO^-] + (m-1)[XOM^{(m-1)}] + (m-2)[(XO)_2M^{(m-2)}] \\ &+ \sum_{i=1}^n (1-i)[XH_{(x-i)}L^{(1-i)}] + \sum_{j=2}^n (2-j)[XH_{2(x-j)}L^{(2-j)}] \end{aligned} \quad (32)$$

This set of equations can be solved by hand or with a computer program using the mathematical approach outlined by Westall (1980).

### Triple Layer Model

The triple layer model was developed at Stanford University (Davis et al., 1978; Davis and Leckie, 1978, 1980; Hayes and Leckie, 1986). The model contains the following assumptions:

- (1) protons and hydroxyl ions form inner-sphere surface complexes



- (2) ion adsorption reactions produce either outer-sphere or inner-sphere surface complexes
- (3) ions from the background electrolyte form outer-sphere complexes
- (4) the Infinite Dilution Reference State determines the activity coefficients of the aqueous species
- (5) three planes of charge represent the oxide surface
- (6) the relationships between surface charges,  $\sigma_o$  and  $\sigma_d$ , and surface potentials,  $\psi_o$ ,  $\psi_\beta$ , and  $\psi_d$ , are:

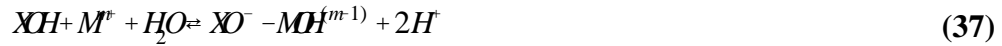
$$\sigma_d = -\frac{Sa}{F} (8\epsilon_o DRTI)^{1/2} \sinh(F\psi_d/2RT) \quad (33)$$

$$\sigma_o = \frac{C_1 Sa}{F} (\psi_o - \psi_\beta) \quad (34)$$

$$\sigma_d = \frac{C_2 Sa}{F} (\psi_d - \psi_\beta) \quad (35)$$

where  $\epsilon_o$  is the permittivity of vacuum, D is the dielectric constant of water, I is the ionic strength, and  $C_1$  and  $C_2$  are capacitance densities.

The equations for inner-sphere surface complexation are Eqs. (19) through (24) as written for the constant capacitance model. The equations for outer-sphere surface complexation are (Davis et al., 1978; Davis and Leckie, 1978, 1980):



where  $C^+$  is the cation and  $A^-$  is the anion of the background electrolyte and outer-sphere

complexes are indicated by splitting the surface complexes with dashes. In the triple layer model an inner-sphere metal surface complex is represented as bidentate, Eq. (22), while an outer-sphere metal surface complex is represented as a hydroxy-metal surface species, Eq. (37). Davis and Leckie (1978). found the outer-sphere hydroxy-metal complexation reaction to be more consistent with their experimental data. For anion surface complexation, Davis and Leckie (1980) found that they could obtain results more consistent with their experimental data by using a protonated outer-sphere surface complex, Eq. (39), instead of a bidentate inner-sphere surface complex, Eq. (24).

The equilibrium constants for inner-sphere surface complexation are Eqs. (25) through (30) as written for the constant capacitance model where  $\psi$  is replaced by  $\psi_o$ . The equilibrium constants for outer-sphere surface complexation are (Davis et al., 1978; Davis and Leckie, 1978, 1980):

$$K_M^1(int) = \frac{[XO^- - M^*][H^+]}{[XH][M^*]} \exp[F(m\psi_\beta - \psi_o)/RT] \quad (42)$$

$$K_M^2(int) = \frac{[XO^- - MH^{(m-1)}][H^+]^2}{[XH][M^*]} \exp[R(m-1)\psi_\beta - \psi_o)/RT] \quad (43)$$

$$K_L^1(int) = \frac{[XH_2^+ - L^{\ell-}]}{[XH][H^+][L^{\ell-}]} \exp[F(\psi_o - \ell\psi_\beta)/RT] \quad (44)$$

$$K_L^2(int) = \frac{[XH_2^+ - LH^{(\ell-1)-}]}{[XH][H^+]^2[L^{\ell-}]} \exp[R\psi_o - (\ell-1)\psi_\beta)/RT] \quad (45)$$

$$K_{C^+}(int) = \frac{[XO^- - C^+][H^+]}{[XH][C^+]} \exp[R\psi_\beta - \psi_o)/RT] \quad (46)$$

$$K_{A^-}(int) = \frac{[XH_2^+ - A^-]}{[XH][H^+][A^-]} \exp[R\psi_o - \psi_\beta)/RT] \quad (47)$$

The mass balance for the surface functional group is:

$$\begin{aligned}
[\text{XH}]_T = & [\text{XH}] + [\text{XH}_2^+] + [\text{XO}^-] + [\text{XOM}^{(m-1)}] + 2[(\text{XO})_2\text{M}^{(m-2)}] \\
& + [\text{XL}^{(\ell-1)-}] + 2[\text{XL}_2^{(\ell-2)-}] + [\text{XO}^- - \text{M}^{\#}] + [\text{XO}^- - \text{MH}^{(m-1)}] \\
& + [\text{XH}_2^+ - \text{L}^{\ell-}] + [\text{XH}_2^+ - \text{LH}^{(\ell-1)-}] + [\text{XO}^- - \text{C}^+] + [\text{XH}_2^+ - \text{A}^-]
\end{aligned} \tag{48}$$

and the charge balances are:

$$\sigma_o + \sigma_\beta + \sigma_d = 0 \tag{49}$$

$$\begin{aligned}
\mathfrak{I}_o = & [\text{XH}_2^+] + [\text{XH}_2^+ - \text{L}^{\ell-}] + [\text{XH}_2^+ - \text{LH}^{(\ell-1)-}] + (m-1)[\text{XOM}^{(m-1)}] \\
& + (m-2)[(\text{XO})_2\text{M}^{(m-2)}] + [\text{XH}_2^+ - \text{A}^-] - [\text{XO}^-] - [\text{XO}^- - \text{M}^{\#}] \\
& - [\text{XO}^- - \text{MH}^{(m-1)}] - (\ell-1)[\text{XL}^{(\ell-1)-}] - (\ell-2)[\text{XL}_2^{(\ell-2)-}] - [\text{XO}^- - \text{C}^+]
\end{aligned} \tag{50}$$

$$\begin{aligned}
\sigma_\beta = & m[\text{XO}^- - \text{M}^{\#}] + (m-1)[\text{XO}^- - \text{MH}^{(m-1)}] + [\text{XO}^- - \text{C}^+] \\
& - \ell[\text{XH}_2^+ - \text{L}^{\ell-}] - (\ell-1)[\text{XH}_2^+ - \text{LH}^{(\ell-1)-}] - [\text{XH}_2^+ - \text{A}^-]
\end{aligned} \tag{51}$$

The above set of equations can be solved with a computer program using the mathematical approach described by Westall (1980).

#### Stern variable-surface charge variable-surface-potential (VSC-VSP) model

The Stern VSC-VSP model of the surface-solution interface was developed in Australia (Bowden et al., 1977; Barrow et al., 1980; Bowden et al., 1980, Barrow et al. 1981; Barrow, 1987). The model contains the following assumptions:

- (1) protons, hydroxyl ions, and "strongly adsorbed" oxyanions and metals form inner-sphere surface complexes
- (2) protons and hydroxyl ions reside in the o-plane close to the surface
- (3) "strongly adsorbed" ions reside in an a-plane a short distance away from the surface o-plane
- (4) major cations and anions form outer-sphere surface complexes and reside in the  $\beta$ -plane a short distance away from the a-plane
- (5) the surface functional group is defined as OH-X-OH<sub>2</sub> allowing only one protonation or dissociation to occur for every two surface hydroxyl groups
- (6) the relationships between surfaces charges,  $\sigma_o$ ,  $\sigma_a$ ,  $\sigma_\beta$ , and  $\sigma_d$ , and surface potentials,  $\psi_o$ ,  $\psi_a$ ,  $\psi_\beta$ , and  $\psi_d$ , are Eq. (33) and:

$$\psi_o - \psi_a = \sigma_o / C_{oa} \tag{52}$$

$$\psi_a - \psi_\beta = (\sigma_o + \sigma_a) / C_{a\beta} \quad (53)$$

$$\psi_\beta - \psi_d = -\sigma_d / C_{\beta d} \quad (54)$$

where  $\sigma_o$ ,  $\sigma_a$ ,  $\sigma_\beta$ , and  $\sigma_d$  have units of  $\text{mol}_c \text{ m}^{-2}$  and  $C_{oa}$ ,  $C_{a\beta}$ , and  $C_{\beta d}$  have units of  $\text{mol}_c \text{ V}^{-1} \text{ m}^{-2}$ . The diffuse layer charge,  $\sigma_d$ , Eq. (33) has units of  $\text{mol}_c \text{ L}^{-1}$  and must be divided by the surface area and the suspension density.

The Stern VSC-VSP model emphasizes parameter optimization and thus defines neither specific surface species nor surface reactions and provides neither equilibrium constant expressions nor mass balance. The charge balance expressions are:

$$\sigma_o + \sigma_a + \sigma_\beta + \sigma_d = 0 \quad (55)$$

$$\sigma_o = \frac{N_s \left\{ K_H^+ [H^+] \exp(-F\psi_o/RT) - K_{OH}^- [OH^-] \exp(F\psi_o/RT) \right\}}{1 + K_H^+ [H^+] \exp(-F\psi_o/RT) + K_{OH}^- [OH^-] \exp(F\psi_o/RT)} \quad (56)$$

$$\sigma_a = \frac{N_T \sum_i Z_i K_i a_i \exp(-Z_i F\psi_a/RT)}{1 + \sum_i K_i a_i \exp(-Z_i F\psi_a/RT)} \quad (57)$$

$$\sigma_\beta = \frac{N_s \left\{ K_{cat} [C^+] \exp(-F\psi_\beta/RT) - K_{an}^- [A^-] \exp(F\psi_\beta/RT) \right\}}{1 + K_{cat} [C^+] \exp(-F\psi_\beta/RT) + K_{an}^- [A^-] \exp(F\psi_\beta/RT)} \quad (58)$$

where  $N_s$  is the maximum surface charge density ( $\text{mol}_c \text{ m}^{-2}$ ),  $N_T$  is the maximum adsorption of specifically adsorbed ions ( $\text{mol}_c \text{ m}^{-2}$ ),  $K_i$ ,  $a_i$ , and  $Z_i$  are the binding constant, the activity, and the charge of the  $i$ th specifically adsorbed ion, respectively.

To solve this set of equations, values of  $N_s$ ,  $N_T$ ,  $K_i$ , and  $C_i$ , are chosen to optimize model fit to the data. Subsequently, the charge densities,  $\sigma_i$ , and the electrostatic potentials,  $\psi_i$ , are calculated using a computer program (Barrow, 1979).

The Stern VSC-VSP model has been extended to describe ion adsorption by soil materials (Barrow, 1983), including the rate of adsorption (Barrow, 1986a). The extended Stern VSC-VSP model contains the following assumptions:

- (1) individual sites react with adsorbing ions as with sites on variable charge oxides
- (2) a range of sites exists whose summed adsorption behavior can be modeled using a distribution of parameters of the Stern VSC-VSP model
- (3) the initial adsorption reaction induces a diffusion gradient into the particle

interior that begins a solid-state diffusion process

The equations for the extended Stern VSC-VSP model describe (Barrow, 1986a):

A) Heterogeneity of the surface:

$$P_j = 1/(\sigma/\sqrt{2\pi}) \exp[-0.5(\psi_{a0j} - \bar{\psi}_{a0}/\sigma)^2] \quad (59)$$

where  $P_j$  is the probability that a particle has initial potential  $\psi_{a0j}$ ,  $\bar{\psi}_{a0}$  is the mean value of  $\psi_{a0j}$ , and  $\sigma$  is the standard deviation of  $\psi_{a0j}$ .

B) Adsorption on each component of the surface:

1) at equilibrium:

$$\theta_j = \frac{K_i \alpha \gamma c \exp(-Z_i F \psi_{aj} / RT)}{1 + K_i \alpha \gamma c \exp(-Z_i F \psi_{aj} / RT)} \quad (60)$$

where  $\theta_j$  is the proportion of the  $j$ th component occupied by the  $i$ th adsorbed ion,  $\psi_{aj}$  is the potential of the  $j$ th component,  $\alpha$  is the fraction of adsorbate present as the  $i$ th ion,  $\gamma$  is the activity coefficient, and  $c$  is the total concentration of adsorbate.

2) rate of adsorption:

$$\theta_{jt} = \frac{K_1^* c (1 - \theta_j) - k_2^* \theta_j}{k_1^* c + k_2^*} [1 - \exp(-t (k_1^* c + k_2^*))] \quad (61)$$

$\theta_{jt}$  is the increment in  $\theta_j$  over time interval  $t$ , and

$$k_1^* = k_1 \alpha \gamma \exp(\bar{\alpha} F \bar{\psi}_{aj} / RT) \quad (62)$$

$$k_2^* = k_2 \alpha \gamma \exp(-\bar{\alpha} F \bar{\psi}_{aj} / RT) \quad (63)$$

where  $k_1$  and  $k_2$  are rate coefficients  $\bar{\alpha}$  and  $\bar{\alpha}$  are transfer coefficients.

C) Diffusive penetration:

$$M_j = 2/\sqrt{\pi} [C_{0j} \sqrt{Df t} + \sum_0^k (C_{kj} - C_{kj-1}) \sqrt{\tilde{D}f_k (t - t_k)}] \quad (64)$$

where  $M_j$  is the amount of material transferred to the interior of the  $j$ th component on an area basis,  $C_{0j}$  is the surface concentration of the adsorbed ion at time  $t$ ,  $C_{kj}$  is the value of  $C_{0j}$  at time  $t_k$ ,  $D$  is the coefficient related to the diffusion coefficient via the thickness of the adsorbed layer, and  $f$  is the thermodynamic factor.

D) Feedback effects on potential:

1) for a single period of measurement:

$$\psi_{aj} = \psi_{a0j} - m_1 \theta_j \quad (65)$$

where  $\psi_{aj}$  is the potential of the  $j$ th component after reaction and  $m_1$  is a parameter.

2) for measurement through time:

$$\psi_{aj} = \psi_{a0j} - m_1 \theta_j - m_2 M / N_{mj} \quad (66)$$

where  $N_{mj}$  is the maximum adsorption on component  $j$  and  $m_2$  is a parameter.

E) Effects of temperature:

$$D = A \exp(-E/RT) \quad (67)$$

where  $E$  is an activation energy and  $A$  is a parameter.

$$K_i = \exp(B/RT) \quad (68)$$

where  $B$  represents potentials in specified standard states plus an interaction term (Bowden et al., 1977).

The continuous distribution of Eq. (59) was divided into thirty discrete elements. The thirty sets of equations were solved iteratively with a computer program using the criterion of goodness-of-fit to ion sorption (Barrow, 1983). Because of the very large number of adjustable parameters, the extended Stern VSC-VSP model should be regarded as a curve-fitting procedure, despite its foundation in chemical principles.

## APPLICATIONS OF CHEMICAL MODELS TO SOIL SYSTEMS

### Constant Capacitance Model

Applications of the constant capacitance model to soil systems have so far been restricted to the description of anion adsorption. The model has been used to describe phosphate (Goldberg and Sposito, 1984), borate (Goldberg and Glaubig, 1986), selenite (Sposito et al., 1988; Goldberg and Glaubig, 1988a), arsenate (Goldberg and Glaubig, 1988b), sulfate (Kooner et al., 1995), and molybdate (Goldberg et al., 1996) adsorption on soils. Values of the protonation and dissociation constants were averages obtained from a literature compilation of  $\log K_+(\text{int})$  and  $\log K_-(\text{int})$  values for aluminum and iron oxide minerals for all studies except that of Kooner et al. (1995). Kooner et al. (1995) obtained  $\log K_+(\text{int})$  and  $\log K_-(\text{int})$  values by optimizing potentiometric titration data using the computer program FITEQL (Westall, 1982). FITEQL is an iterative nonlinear least squares optimization program designed to fit equilibrium constants to experimental data and contains the constant capacitance model and the triple layer model. Capacitance values for the soil studies ranged from  $1.06 \text{ F m}^{-2}$  (Goldberg and Sposito, 1984) to  $2.7 \text{ F m}^{-2}$  (Sposito et al., 1988).

Monodentate anion surface species as defined in Eq. (23) were used in all of the above studies. Sposito et al. (1988) assumed that monodentate selenite species are formed on one set of surface sites and bidentate selenite species are formed on another set of surface

sites. Anion surface complexation constants for all studies were optimized using the FITEQL computer program. To describe borate (Goldberg and Glaubig, 1986) and selenite (Goldberg and Glaubig, 1988a) adsorption, values of  $\log K_+(\text{int})$  and  $\log K_-(\text{int})$  were optimized along with the anion surface complexation constants. The optimized value of  $\log K_-(\text{int})$  for some of the soils was insignificantly small. This is a chemically unrealistic situation that potentially reduces the application of the model to a curve-fitting procedure.

The predictive capability of the constant capacitance model to describe ion adsorption has been tested for phosphate (Goldberg and Sposito, 1984), borate (Goldberg and Glaubig, 1986), and selenite (Sposito, 1998). Sposito (1988) were able to qualitatively predict selenite adsorption on four soils using the selenite surface complexation constants obtained for one other soil. Using an average set of surface complexation constants obtained from numerous soils, the model qualitatively predicted phosphate (Goldberg and Sposito, 1984) and borate (Goldberg and Glaubig, 1986) adsorption on individual soils.

### Triple Layer Model

The triple layer model has been applied to calcium, magnesium, sulfate (Charlet, 1986; Charlet and Sposito, 1987, 1989; Charlet et al., 1993), chromate (Zachara et al., 1989), and molybdate (Goldberg et al., 1996) adsorption on soils. Charlet (1986; Charlet and Sposito, 1987) carried out potentiometric titrations and measured background electrolyte adsorption on a Brazilian oxisol. From these experiments they were able to extrapolate values of the protonation and dissociation constants and the surface complexation constants for the background electrolyte.

Charlet (1986; Charlet and Sposito, 1989) found good fits of the triple layer model to calcium, magnesium, and sulfate adsorption on a Brazilian oxisol using monodentate inner-sphere surface complexes and their experimentally determined values of  $\log K_+(\text{int})$ ,  $\log K_-(\text{int})$ ,  $\log K_{C+}(\text{int})$ , and  $\log K_{A-}(\text{int})$ . Charlet et al. (1993) on the other hand described sulfate adsorption on an acidic forest soil as a monodentate outer-sphere surface complex by using literature values of  $\log K_+(\text{int})$ ,  $\log K_-(\text{int})$ ,  $\log K_{C+}(\text{int})$ , and  $\log K_{A-}(\text{int})$  that had been determined for goethite (Hsi and Langmuir, 1985). The justification provided was that the clay components of the soil consisted of phyllosilicates and iron oxide minerals. In a similar approach, Zachara et al. (1989) used literature values of  $\log K_+(\text{int})$ ,  $\log K_-(\text{int})$ ,  $\log K_{C+}(\text{int})$ , and  $\log K_{A-}(\text{int})$  that had been determined for an aluminum-substituted goethite (Ainsworth et al., 1989) to describe chromate adsorption as a monodentate outer-sphere surface complex by two soils. These authors assumed that chromate adsorbed only on the iron sites. Goldberg et al. (1996), on the other hand, used literature values of  $\log K_+(\text{int})$ ,  $\log K_-(\text{int})$ ,  $\log K_{C+}(\text{int})$ , and  $\log K_{A-}(\text{int})$  obtained for  $\gamma\text{-Al}_2\text{O}_3$  (Sprycha, 1989a, b) to describe molybdate adsorption on two arid-zone soils using both inner-sphere and outer-sphere adsorption mechanisms. The assumptions were made that the aluminol group is the molybdate reactive functional group in these soils and that its surface complexation reactions can be described with constants for the reactive surface hydroxyls of  $\gamma\text{-Al}_2\text{O}_3$ .

### Stern variable-surface charge variable-surface potential (VSC-VSP) model

The extended Stern VSC-VSP model has been used to describe the effect of time and temperature on fluoride, molybdate (Barrow, 1986a), zinc (Barrow, 1986b), selenite,

and selenate (Barrow and Whelan, 1989b) adsorption, the effect of pH on phosphate (Barrow, 1984, 1986d), zinc (Barrow, 1986c, d), fluoride (Barrow and Ellis, 1986), selenite, selenate (Barrow and Whelan, 1989a), and borate (Barrow, 1989) adsorption, and the effect of ionic strength on selenite, selenate (Barrow and Whelan, 1989a), and borate (Barrow, 1989) adsorption on Australian soils. Because of its very large number of adjustable parameters, the Stern VSC-VSP model was able to provide a good fit to the experimental data for all of the above cases. In the description of the effect of pH on phosphate (Barrow, 1984) and zinc (Barrow, 1986c) adsorption on soils, binding constants obtained previously for goethite were used.

## ADVANTAGES OF CHEMICAL MODELS

The major advantage of the chemical models is that they consider the surface charge resulting from the protonation-dissociation reactions and from the ion surface complexation reactions. The surface complexation models are descriptions of adsorption phenomena whose molecular features can be given thermodynamic significance (Sposito, 1983). However, goodness-of-fit to experimental adsorption data cannot be used as evidence for the presence of any of the surface complexes postulated in the chemical models.

As the complexity of a model increases, the number of adjustable parameters also increases, improving its curve-fitting ability. Chemical significance of the model application suffers when parameters whose value are available experimentally are adjusted. Such is the case for the maximum surface charge density and the maximum ion adsorption density in the Stern VSC-VSP model. The Stern VSC-VSP model is also compromised chemically because no mass balance is carried out for the surface functional group. Until such time as independent experimental evidence allows the determination of the exact structure of adsorbed surface complexes, chemical simplicity and a small number of adjustable parameters are preferable.

## APPROXIMATIONS IN THE USE OF CHEMICAL MODELS IN SOIL SYSTEMS

The chemical models described above contain the assumption that ion adsorption takes place at one or at most two sets of reactive surface sites. Clearly, soils are complex multisite mixtures having a variety of reactive surface functional groups. Thus the equilibrium constants determined for soils represent average composite values for all sets of reactive functional groups.

The total number of reactive surface functional groups,  $[SOH]_T$  is an important parameter in the chemical models and is related to the surface site density,  $N_s$ , by the following expression:

$$[SOH]_T = \frac{S a 10^{18}}{N_A} N_s \quad (69)$$

where  $N_A$  is Avogadro's number and  $N_s$  has units of sites  $\text{nm}^{-2}$ . In the application of chemical models to soils, surface site density values have been obtained using maximum ion adsorption (Goldberg and Sposito, 1984) or optimized to fit the experimental data (Barrow, 1983). To allow standardization of surface complexation modeling and development of a



self-consistent thermodynamic database, Davis and Kent (1990) recommended use of a surface site density value of 2.31 sites nm<sup>-2</sup> for all natural adsorbents including soils.

In the application of the surface complexation models to soils dominant in clay minerals, the assumption is made that ion adsorption occurs on the aluminol and silanol groups on the clay edges. The effect of the permanent charge sites on this reaction is not considered. This simplification may be inappropriate, especially for anions, since repulsive electrostatic forces emanating from particle faces may spill over and affect adsorption on the clay edges (Secor and Radke, 1985).

## REFERENCES

- Ainsworth, C.C., D.C. Girvin, J.M. Zachara, and S.C Smith. 1989. Chromate adsorption on goethite: Effects of aluminum substitution. *Soil Sci. Soc. Am. J.* 53:411-418.
- Barrow, N.J. 1978. The description of phosphate adsorption curves. *J. Soil Sci.* 29:447-462.
- Barrow, N.J. 1979. Computer programmes for calculating charge and adsorption of ions in variable charge surfaces. Technical Memorandum 79/3. CSIRO. Division of Land Resources Management. Perth, Australia.
- Barrow, N.J. 1983. A mechanistic model for describing the sorption and desorption of phosphate by soil. *J. Soil Sci.* 34:733-750.
- Barrow, N.J. 1984. Modelling the effects of pH on phosphate sorption by soils. *J. Soil Sci.* 35:283-297.
- Barrow, N.J. 1986a. Testing a mechanistic model. I. The effects of time and temperature on the reaction of fluoride and molybdate with a soil. *J. Soil Sci.* 37:267-275.
- Barrow, N.J. 1986b. Testing a mechanistic model. II. The effects of time and temperature on the reaction of zinc with a soil. *J. Soil Sci.* 37:277-286.
- Barrow, N.J. 1986c. Testing a mechanistic model. IV. Describing the effects of pH on zinc retention by soils. *J. Soil Sci.* 37:295-302.
- Barrow, N.J. 1986d. Testing a mechanistic model. VI. Molecular modelling of the effects of pH on phosphate and on zinc retention by soils. *J. Soil Sci.* 37:311-318.
- Barrow, N.J. 1987. Reactions with variable-charge soils. Martinus Nijhoff, Dordrecht, Netherlands.
- Barrow, N.J. 1989. Testing a mechanistic model. X. The effect of pH and electrolyte concentration on borate sorption by a soil. *J. Soil Sci.* 40:427-435.
- Barrow, N.J., J.W. Bowden, A.M. Posner, and J.P. Quirk. 1980. An objective method for fitting models of ion adsorption on variable charge surfaces. *Aust. J. Soil Res.* 18:37-47.
- Barrow, N.J., J.W. Bowden, A.M. Posner, and J.P. Quirk. 1981. Describing the adsorption of copper, zinc and lead on a variable charge mineral surface. *Aust. J. Soil Res.* 19:309-321.
- Barrow, N.J., and A.S. Ellis. 1986. Testing a mechanistic model. III. The effects of pH on fluoride retention by a soil. *J. Soil Sci.* 37:287-293.
- Barrow, N.J., and B.R. Whelan. 1989a. Testing a mechanistic model. VII. The effects of pH and of electrolyte on the reaction of selenite and selenate with a soil. *J. Soil Sci.* 40:17-28.

- Barrow, N.J., and B.R. Whelan. 1989b. Testing a mechanistic model. VIII. The effects of time and temperature of incubation on the sorption and subsequent desorption of selenite and selenate by a soil. *J. Soil Sci.* 40:29-37.
- Bowden, J.W., A.M. Posner, and J.P. Quirk. 1977. Ionic adsorption on variable charge mineral surfaces. Theoretical-charge development and titration curves. *Aust. J. Soil Res.* 15:121-136.
- Bowden, J.W., S. Nagarajah, N.J. Barrow, A.M. Posner, and J.P. Quirk. 1980. Describing the adsorption of phosphate, citrate and selenite on a variable charge mineral surface. *Aust. J. Soil Res.* 18:49-60.
- Charlet, L. 1986. Adsorption of some macronutrient ions on an oxisol. An application of the triple layer model. Ph.D. Thesis. University of California, Riverside, CA.
- Charlet, L., N. Dise, and W. Stumm. 1993. Sulfate adsorption on a variable charge soil and on reference minerals. *Agric. Ecosystems & Environment* 47:87-102.
- Charlet, L., and G. Sposito. 1987. Monovalent ion adsorption by an oxisol. *Soil Sci. Soc. Am. J.* 51:1155-1160.
- Charlet, L., and G. Sposito. 1989. Bivalent ion adsorption by an oxisol. *Soil Sci. Soc. Am. J.* 53:691-695.
- Davis, J.A., R.O. James, and J.O. Leckie. 1978. Surface ionization and complexation at the oxide/water interface. I. Computation of electrical double layer properties in simple electrolytes. *J. Colloid Interface Sci.* 63:480-499.
- Davis, J.A., and J.O. Leckie. 1978. Surface ionization and complexation at the oxide/water interface. II. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. *J. Colloid Interface Sci.* 67:90-107.
- Davis, J.A., and J.O. Leckie. 1980. Surface ionization and complexation at the oxide/water interface. 3. Adsorption of anions. *J. Colloid Interface Sci.* 74:32-43.
- Dowd, J.E., and D.S. Riggs. 1965. A comparison of estimates of Michaelis-Menton kinetic constants from various linear transformations. *J. Biol. Chem.* 240:863-869.
- Goldberg, S., and H.S. Forster. 1991. Boron sorption on calcareous soils and reference calcites. *Soil Sci.* 152:304-310.
- Goldberg, S., and R.A. Glaubig. 1986. Boron adsorption on California soils. *Soil Sci. Soc. Am. J.* 50:1173-1176.
- Goldberg, S., and R.A. Glaubig. 1988a. Anion sorption on a calcareous, montmorillonitic soil - selenium. *Soil Sci. Soc. Am. J.* 52:954-958.
- Goldberg, S., and R.A. Glaubig. 1988b. Anion sorption on a calcareous, montmorillonitic soil - arsenic. *Soil Sci. Soc. Am. J.* 52:1297-1300.
- Goldberg, S., and G. Sposito. 1984. A chemical model of phosphate adsorption by soils: II. Noncalcareous soils. *Soil Sci. Soc. Am. J.* 48:779-783.
- Goldberg, S., C. Su, and H.S. Forster. 1996. Sorption of molybdenum on oxides, clay minerals, and soils: Mechanisms and Models. *Am. Chem. Soc. Symp. Proc.* (in review).
- Hayes, K.F., and J.O. Leckie. 1986. Mechanism of lead ion adsorption at the goethite-water interface. *Am. Chem. Soc. Symp. Ser.* 323:114-141.
- Hohl, H., and W. Stumm. 1976. Interaction of  $Pb^{2+}$  with hydrous  $\gamma-Al_2O_3$ . *J. Colloid Interface Sci.* 55:281-288.

- Hsi, C.-K.D., and D. Langmuir. 1985. Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. *Geochim. Cosmochim. Acta* 49:1931-1941.
- Kinniburgh, D.G. 1985. ISOTHERM. A computer program for analyzing adsorption data. Report WD/ST/85/02. Version 2.2. British Geological Survey, Wallingford, UK.
- Kinniburgh, D.G. 1986. General purpose adsorption isotherms. *Environ. Sci. Technol.* 20:895-094.
- Kooner, Z.S., P.M. Jardine, and S. Feldman. 1995. Competitive surface complexation modeling of sulfate and natural organic carbon on soil. *J. Environ. Qual.* 24:656-662.
- Reardon, E.J. 1981.  $K_d$ 's — Can they be used to describe reversible ion sorption reactions in contaminant migration? *Groundwater* 19:279-286.
- Schindler, P.W., and H. Gamsjäger. 1972. Acid-base reactions of the  $\text{TiO}_2$  (anatase)-water interface and the point of zero charge of  $\text{TiO}_2$  suspensions. *Kolloid-Z. u. Z. Polymere* 250:759-763.
- Schindler, P.W., B. Fürst, R. Dick, and P.U. Wolf. 1976. Ligand properties of surface silanol groups. I. Surface complex formation with  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$ . *J. Colloid Interface Sci.* 55:469-475.
- Secor, R.B., and C.J. Radke. 1985. Spillover of the diffuse double layer on montmorillonite particles. *J. Colloid Interface Sci.* 103:237-244.
- Sposito, G. 1982. On the use of the Langmuir equation in the interpretation of "adsorption" phenomena: II. The "two-surface" Langmuir equation. *Soil Sci. Soc. Am. J.* 46:1147-1152.
- Sposito, G. 1983. Foundations of surface complexation models of the oxide-aqueous solution interface. *J. Colloid Interface Sci.* 91:329-340.
- Sposito, G. 1984. *The surface chemistry of soils.* Oxford Univ. Press, Oxford, UK.
- Sposito, G. 1989. *The chemistry of soils.* Oxford Univ. Press, Oxford, UK.
- Sposito, G., J.C.M. deWit, and R.H. Neal. 1988. Selenite adsorption on alluvial soils: III. Chemical modeling. *Soil Sci. Soc. Am. J.* 52:947-950.
- Sprycha, R. 1989a. Electrical double layer at alumina/electrolyte interface. I. Surface charge and zeta potential. *J. Colloid Interface Sci.* 127:1-11.
- Sprycha, R. 1989b. Electrical double layer at alumina/electrolyte interface. II. Adsorption of supporting electrolytes. *J. Colloid Interface Sci.* 127:12-25.
- Stumm, W., H. Hohl, and F. Dalang. 1976. Interaction of metal ions with hydrous oxide surfaces. *Croatica Chem. Acta* 48:491-504.
- Stumm, W., R. Kummert, and L. Sigg. 1980. A ligand exchange model for the adsorption of inorganic and organic ligands at hydrous oxide interfaces. *Croatica Chem. Acta* 53:291-312.
- Travis, C.C., and E.L. Etnier. 1981. A survey of sorption relationships for reactive solutes in soil. *J. Environ. Qual.* 10:8-17.
- Veith, J.A., and G. Sposito. 1977. On the use of the Langmuir equation in the interpretation of "adsorption" phenomena. *Soil Sci. Soc. Am. J.* 414:697-702.
- Westall, J. 1980. Chemical equilibrium including adsorption on charged surfaces. *Am. Chem. Soc. Adv. Chem. Ser.* 189:33-44.

- Westall, J.C. 1986. Reactions at the oxide-solution interface: Chemical and electrostatic models. *Am. Chem. Soc. Symp. Ser.* 323:54-78.
- Zachara, J.M., C.C. Ainsworth, C.E. Cowan, and C.T. Resch. 1989. Adsorption of chromate by subsurface soil horizons. *Soil Sci. Soc. Am. J.* 53:418-428.